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P. 15Production of Oxygen From Lunar Ilmenite

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Abstract

The overall objective of this project is to develop a novel carbothermal reduction process for production of oxygen from lunar ilmenite. The specific objective is to use a reaction sequence in which a wide variety of carbonaceous compounds (including carbonaceous wastes) can be used as reducing agents. During the first phase of this work, two reactor systems were designed, constructed, and operated to investigate the fundamentals of the reactions important in this process. One system is a small fluidized bed, and the other is a thermo-gravimetric reactor system. Preliminary experiments on synthetic ilmenite are conducted to study the effect of carbon type, carbon loading, temperature, and gas flow rate. Results indicate that a reaction path based on carbon gasification can be employed to promote the overall kinetics. A unique temperature and concentration-programmed reaction procedure is being developed for rapid parametric study of the process.

Introduction

Oxygen is a consumable material which needs to be produced continuously in most space missions. Its use for propulsion, as well as life support, makes oxygen one of the largest volume chemicals to be produced in space. Production of oxygen from lunar materials is of particular interest and is a very attractive possibility.

There is a significant amount of oxygen on the moon, although very little is readily available as water or gaseous oxygen. The only practical source of oxygen on the lunar surface is igneous materials, which contain typically 40-50% oxygen as oxides. Minerals present in these rocks include ilmenite (the most abundant opaque material in lunar rocks), anorthite, and olivine. The igneous rocks have been pre-crushed to form regolith, the lunar equivalent of soil, by meteoritic bombardments. This reduces the need for crushing and simplifies the mining and separation problem greatly.<sup>1,2</sup>

Extraction of oxygen from iron oxide present in lunar ilmenite is of particular interest because it is energetically more favorable than extraction from silicon, aluminum, titanium, calcium, or magnesium oxides. Iron oxide reduction is also attractive because of its potential for producing iron as a co-product. A number of processes have been suggested for oxygen production from ilmenite in lunar regolith. Table 1.1 shows a list of these processes. Most of these processes require imported

reagents to be recycled in the process. Therefore, low loss per mass is a critical factor and requirement for process feasibility.

Table 1.1. Selected proposed processes.

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Hydrogen reduction

Low-temperature carbothermal reduction

Slagging (high-temperature) carbothermal reduction

Slag electrolysis

Leaching: Fluoroacid

HCl

Caustic

Carbo-chlorination

Vaporization/rapid quenching, arc electrolysis, plasma reduction, alkali metal thermal cycling, vapor-phase pyrolysis, etc.

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Among the proposed processes, the hydrogen and carbothermal reductions of ilmenite appear very promising. Hydrogen reduction has a relatively simple process configuration; the individual steps are relatively well studied. However, the major problem is the large heating and cooling loads required to condense the water and then heat the hydrogen to its reaction temperature. Handling and storage of large amounts of hydrogen is also a problem. Hydrogen reduction of lunar ilmenite has been studied by several investigators.<sup>3</sup> Carbothermal reduction of terrestrial ilmenite has also been extensively studied, but the application to lunar ilmenite is still an open area for investigation.<sup>4</sup>

Even though a considerable body of literature has been published on various aspects of the reduction of terrestrial ilmenite, the mechanism of transformation and the rate-controlling step in the overall reduction have not been clearly established. Most studies on terrestrial ilmenite show that both hydrogen reduction reactions take place in two main stages. In the first stage, the ferric iron component of the ilmenite was rapidly reduced to ferrous iron. In the second stage, which was much slower than the first stage, the ferrous iron was reduced to the metallic state. During the carbothermal process, terrestrial ilmenite starts to react at about 860°C at the contact points between the reactants. Up to 1020°C, solid-state reduction appears to be the main reaction mechanism, while above this temperature, a rate increase has been observed and has been contributed to a change in the mechanism to a gaseous reduction of ilmenite by

regenerated CO.<sup>5,6</sup> It has been reported that the reaction rate between synthetic ilmenite and graphite is increased significantly by the addition of ferric chloride, which promotes the nucleation of iron, and is decreased by the addition of rutile.

The above mechanisms and the available kinetic information are not directly applicable to lunar ilmenite, which is very different from terrestrial ilmenite in both physical and chemical properties. Moreover, the emphasis in reduction of terrestrial ilmenite has been on metal oxide recovery and not on oxygen production. However, the existing technical background on carbothermal processing of terrestrial ilmenite indicates that its application to lunar ilmenite should be pursued. In comparison with the hydrogen reduction, the carbothermal process has a more complicated flow configuration, but is energetically more favorable, and can potentially use a wide variety of carbonaceous compounds as reducing agents. A comparison of the primary features of the carbothermal and hydrogen reduction processes can be made using Tables 1.2 and 1.3.

Table 1.2. Hydrogen reduction.

Advantages
Simple flow sheet
Relatively well-known chemistry
Continuous operation
Disadvantages
Low hydrogen utilization
Problems in hydrogen transport, handling, and storage
High heating/cooling demand
No useful co-products (low integration value)
Key Research Areas
High-temperature water dissociation
High-temperature ceramic membranes
Sensitivity to the physical and chemical properties of the feed
Process design

Table 1.3. Carbothermal reduction.

Advantages
Known technology for terrestrial ilmenite
Available carbonaceous makeup
Almost 100% utilization of carbon
Useful co-products (high integration value)
Ease of carbon transport, storage, and handling
Disadvantages
More complex flow sheet
More solid handling in continuous operation
Key Research Areas
Reaction kinetics and mechanism for lunar ilmenite
Ceramic membranes application
CO <sub>2</sub> reverse fuel cell
Sensitivity to the physical and chemical properties of the feed
Process Design

### Objectives

The overall objectives of this study can be described as follows:

- Study of the mechanism and kinetics of carbothermal reduction of simulated lunar ilmenite; determination of the rate-limiting steps; investigation of the effect of impurities, particularly magnesium; search for catalysts suitable for enhancement of the rate-limiting steps.
- Development of new reduction methods which are based on the use of a waste carbonaceous compound as a carbon source for the process; development of a novel carbothermal reaction path which utilizes gasification of a carbonaceous solid for reducing gaseous species (hydrocarbons and carbon monoxide) to facilitate the reduction reaction kinetics and make the process more flexible in using various forms of carbonaceous feeds.
- Development of advanced gas separation techniques, including the use of high-temperature ceramic membranes.
- Development of an optimized process flow sheet for carbothermal reduction and comparison of this process with the hydrogen reduction scheme, as well

as a general comparison with other leading oxygen production schemes; use of new and advanced material processing and separation techniques.

#### Method of Approach

In the first phase of the work, the emphasis has been on the development of experimental methods for studying the kinetics and mechanism of reduction of simulated lunar ilmenite. The experimental facilities and procedures are summarized below.

*Experimental Apparatus.* Two reactor systems have been designed, fabricated, and put into operation during the past 9 months: A mini-fluidized bed reactor for quick response times and a thermo-gravimetric reactor system with an electronic microbalance for the continuous measurement of rate and sample conversion. Schematic diagrams of these two reactor systems are given in Figures 1.5, 1.6, and 1.7. The components of these two reactor systems are described below.

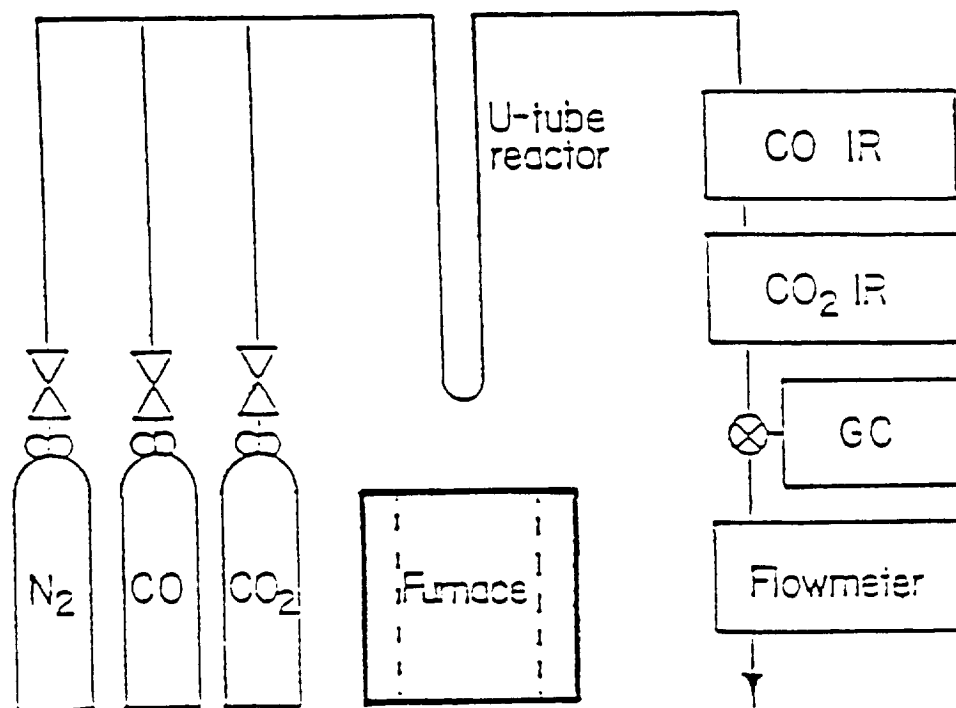


Figure 1.5. Mini-fluidized bed reactor system.

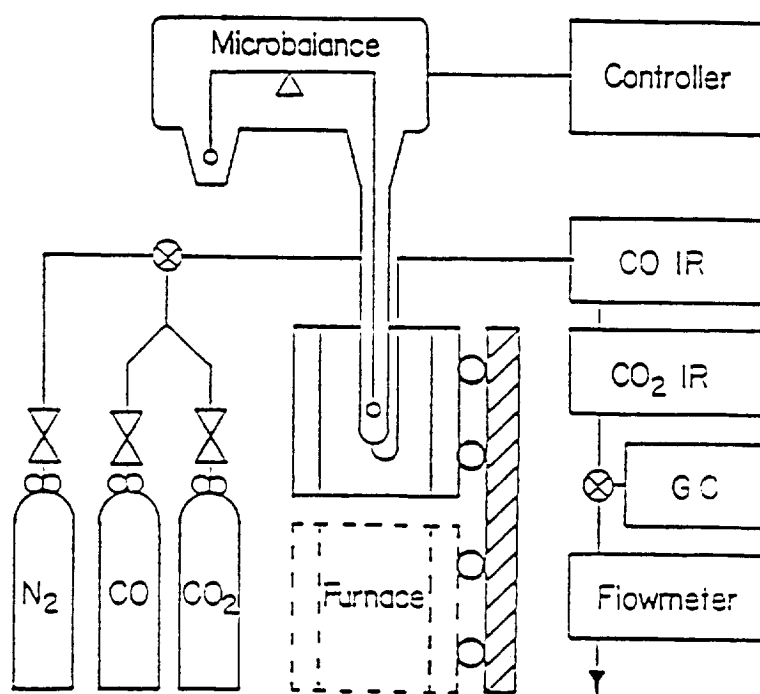


Figure 1.6. Micro-gravimetric reactor system.

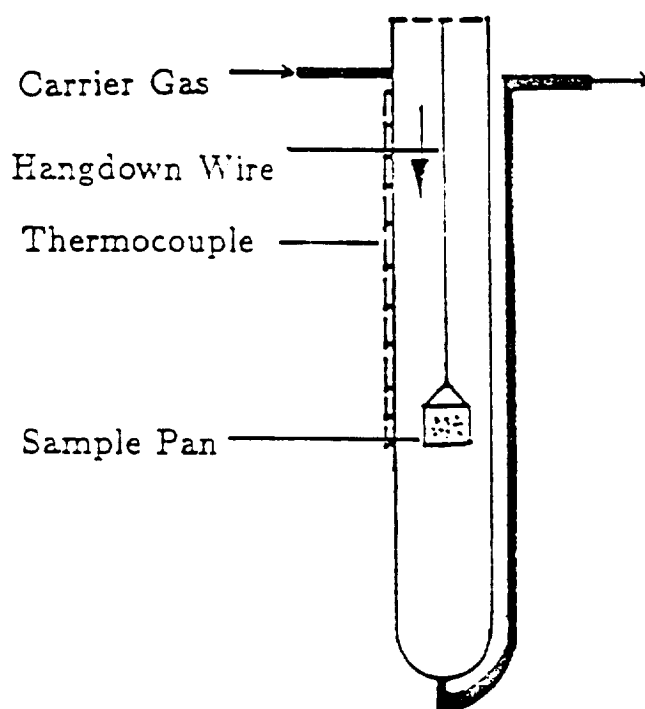


Figure 1.7. Schematic of the quartz reactor.

- a. Gas Preparation Section: This includes a UHP nitrogen delivery system with critical flow elements for mass flow control.
- b. The Mini-Fluidized Bed Reactor: This is a quartz reactor with a U configuration. The reactor is mounted on the stand and can be moved vertically in and out of an electric furnace. A chromel/alumel type K thermocouple is placed adjacent to the fluidized bed to monitor the temperatures independently during the course of an experiment. The ilmenite particles are supported by a stainless steel screen fitted inside the reactor. This reactor has low dead volume and a very rapid response.
- c. Thermo-Gravimetric Reactor: In this reactor system, the sample is suspended on one arm of an electronic recording balance. A specially designed quartz reactor, which surrounds the sample with ports for inlet and dilution gas entry, is mounted vertically on wheels. This configuration allowed rapid start-up and quenching of the experiments for accurate measurement of initial and instantaneous rates. The furnace is equipped with a PID controller for both steady and temperature-programmed reactions.
- d. Gas Analysis Section: This includes nondispersive infrared analyzers for measurement of carbon monoxide and carbon dioxide, as well as a gas chromatograph for a more complete gas analysis.
- e. Other facilities used in our experimental study include an X-ray diffraction spectrometer, Mossbauer spectrometer, and scanning electron microscope with EDX.

*Experimental Procedure.* The work so far has focused on the study of the mechanism and kinetics of reactions important for carbothermal reduction of lunar ilmenite. The samples used have been synthetic ilmenite (iron titanate) obtained from CERAC, Inc., with a purity of 99.9% and particle size between 63 and 74 microns. To simulate lunar ilmenite, it was important to make sure that the iron in the sample was only  $\text{Fe}^{++}$ . To confirm this, Mossbauer spectroscopy was performed on the synthetic ilmenite. A typical Mossbauer spectra of the sample is shown in Figure 1.8. The results indicate that the amount of impurities, including  $\text{Fe}^{+++}$ , was less than 0.8% on a metal basis.

In each experimental run, a well-characterized mixture of ilmenite and carbon with known particle size and composition was placed in the reactor while the furnace was heated to a desired temperature. The gas flow inside the reactor was then stabilized and maintained for purging the reactor and the sample while the furnace temperature approached the pre-set value. To start the run, the reactor was lowered into the furnace

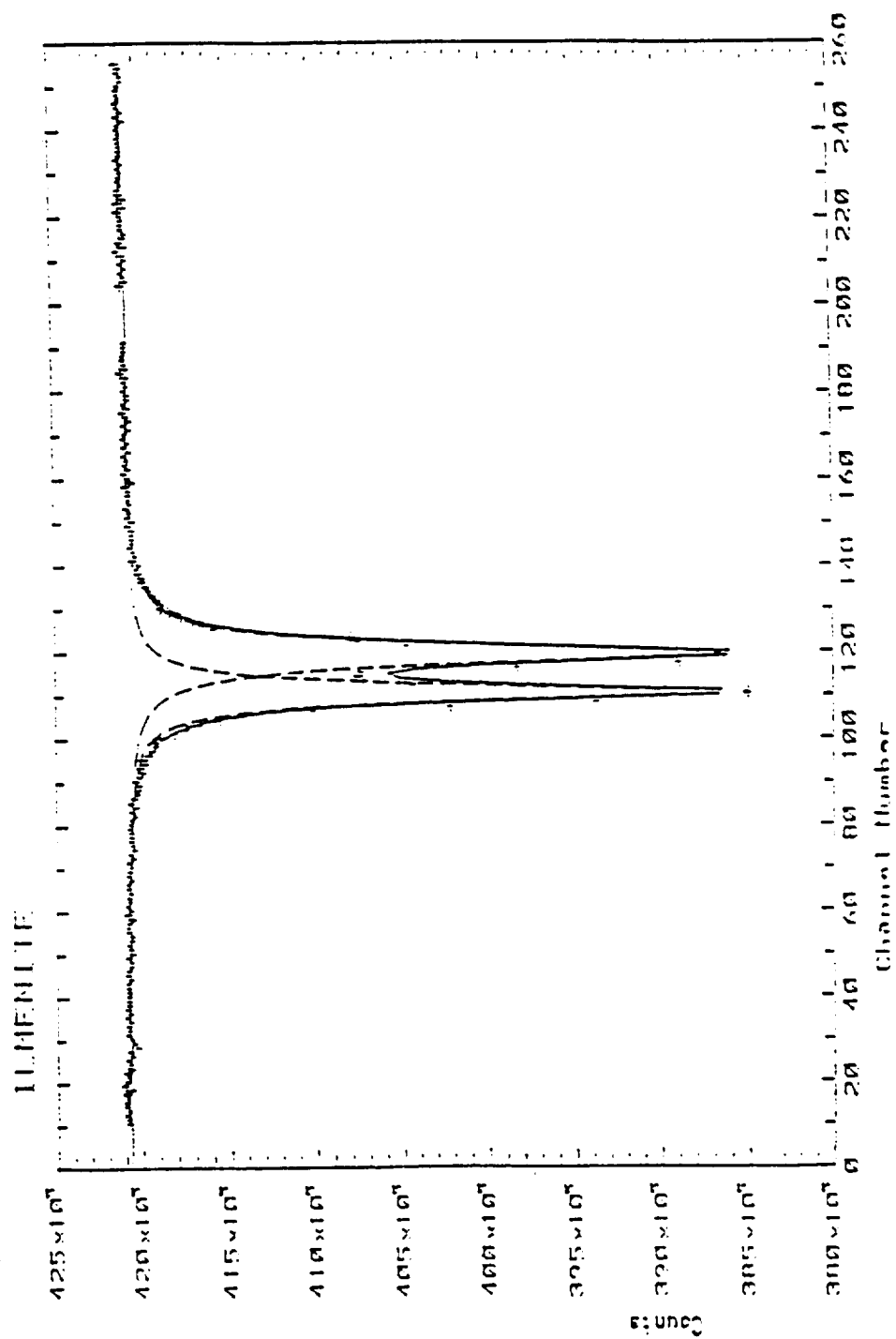


Figure 1.8. Mossbauer velocity spectrum for synthetic ilmenite particles.



(in the fluidized bed system) or the furnace was raised around the reactor (in the thermo-gravimetric system). The course of the reaction was studied by monitoring the gas composition and the sample weight in the gravimetric reactor.

The other methods used for characterization of the starting ilmenite were scanning electron microscopy and X-ray diffraction spectroscopy. Application of these techniques to samples at different levels of conversion can help us to understand the morphological and phase changes that occur in the samples during the course of reaction.

### Discussion of Results

Due to the heterogeneous nature of the reduction reactions, the kinetics of the process depend on the physical structure of the solid. Figures 1.9 and 1.10 are the micrographs of the original synthetic ilmenite. The small particles on the surface are tiny chips generated during the grinding process. Figures 1.11 and 1.12 show partially reacted samples and, in particular, the porosity developed during the reaction. The SEM micrographs show a significant change in the structure and porosity of the particles as the reduction reaction proceeds. It appears that the new products formed on the surface of the particles have a lower melting point compared with that of ilmenite (melting point of iron titanate is  $1327^{\circ}\text{C}$ ). Further characterization of this phase change is in progress.

So far, two types of experiments have been performed in the reactor systems. Most of the results are tests of the accuracy, reproducibility, and calibration of the newly developed reactor systems. More recently, however, experiments for determining the kinetics and mechanisms have been started. Among the first type of experiments are tests of the differential nature of the reactors. This is important to make sure that the kinetics are characteristics of the reaction and not the reactor geometry; this is an important point often neglected in similar studies. As an example, tests with different sample mass were conducted and the initial rates were compared. The results are shown in Table 1.4. The fact that the initial rate did not change significantly with sample size confirms that the reactor is differential and that the rates are intrinsic values. Similar results were obtained when flow rate was varied.

One of the important process parameters is the optimum carbon/ilmenite ratio in the reactor. The preliminary results are shown in Figure 1.13. It appears that the initial rate increases slightly with an increase in the carbon content. The significant difference is in the rate profile. As carbon content decreases, the variations in rate with time and conversion become more significant. The variations in rate are very important in the design of a large-scale reactor.

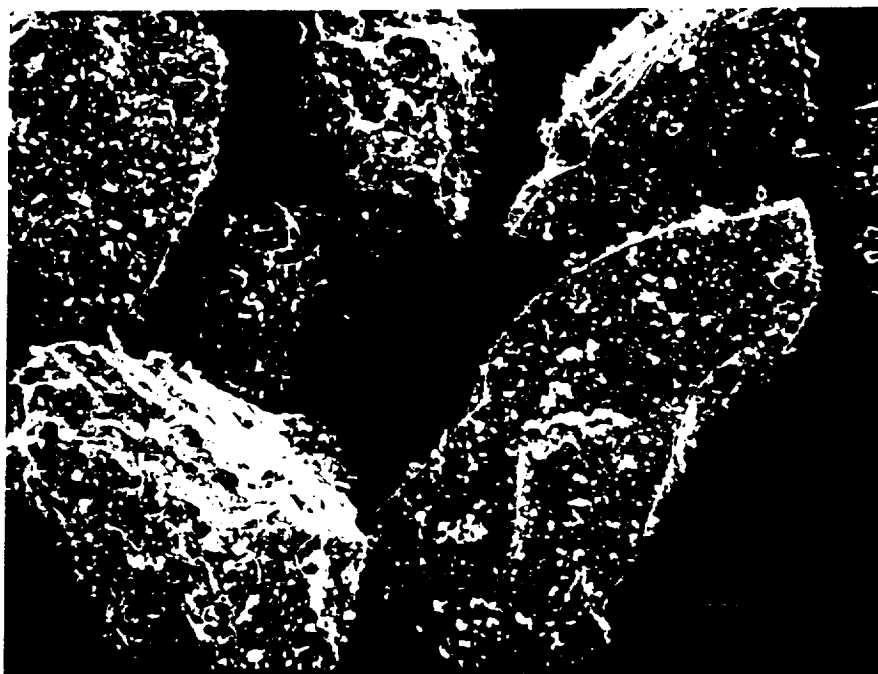


Figure 1.9. The surface microstructure of synthetic ilmenite (particle size  $\cong 70 \mu\text{m}$ ; sample coated with Au/pd); specimen tilt,  $30^\circ$ ; magnification, 600X; left bar length,  $10 \mu\text{m}$ .

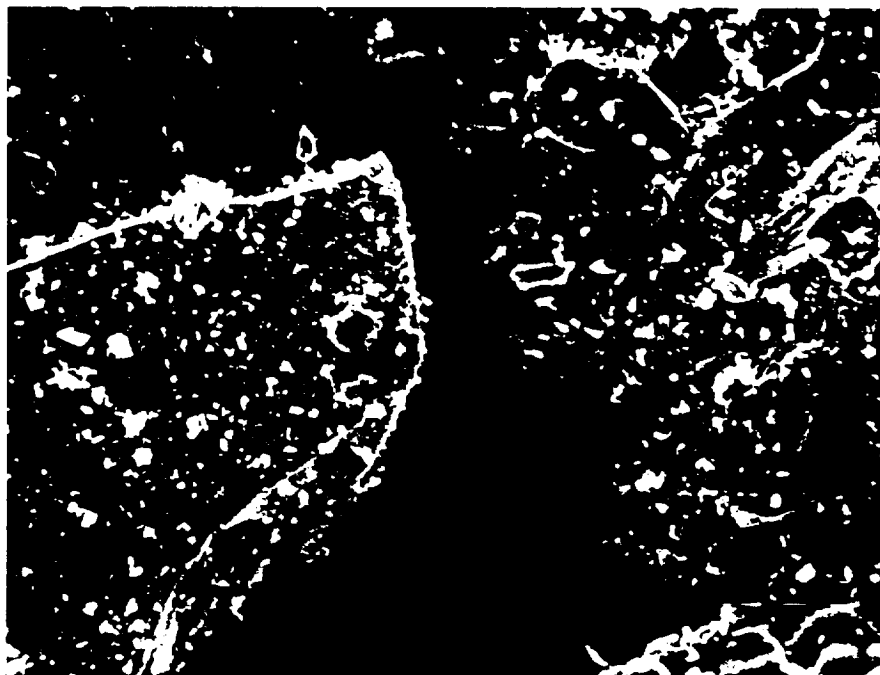


Figure 1.10. The surface microstructure of synthetic ilmenite (particle size  $\cong 70 \mu\text{m}$ ; sample coated with Au/pd); specimen tilt,  $30^\circ$ ; magnification, 1030X; left bar length,  $10 \mu\text{m}$ .

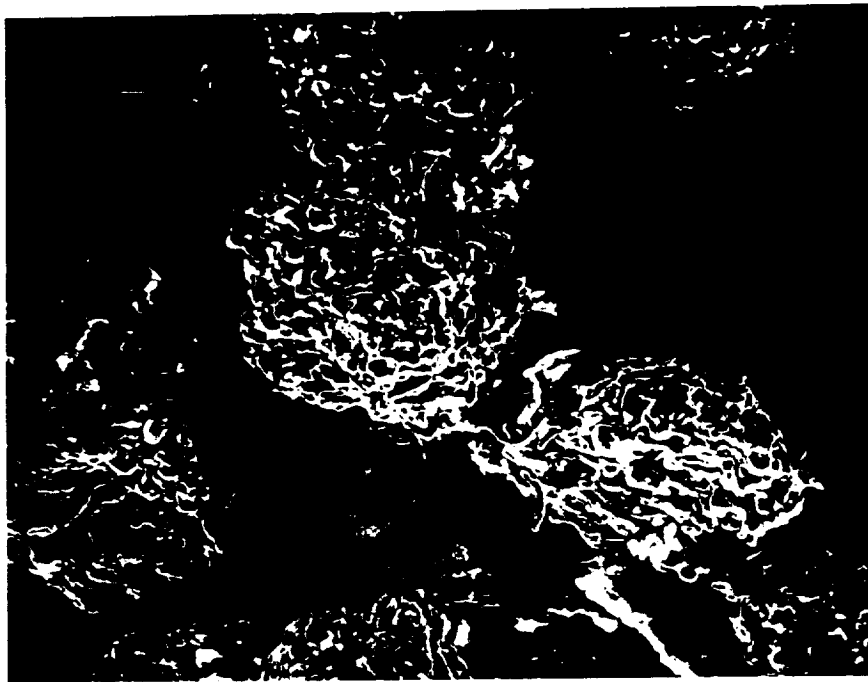


Figure 1.11. The surface microstructure of the reduced synthetic ilmenite (particle size  $\cong 70 \mu\text{m}$ ; sample coated with Au/pd); specimen tilt,  $30^\circ$ ; magnification, 490X; left bar length,  $10 \mu\text{m}$ .



Figure 1.12. The surface microstructure of the reduced synthetic ilmenite (particle size  $\cong 70 \mu\text{m}$ ; sample coated with Au/pd); specimen tilt,  $30^\circ$ ; magnification, 1050X; left bar length,  $10 \mu\text{m}$ .

Table 1.4. Effect of sample mass on reaction kinetics (temperature = 1120°C; flow rate = 75 cc/min).

Run Number	Sample Size (g)	Carbon Content (wt%)	Initial Rate (g CO/g ilmenite·s)
1	0.986	20	$3.3 \times 10^{-4}$
2	0.498	20	$3.1 \times 10^{-4}$

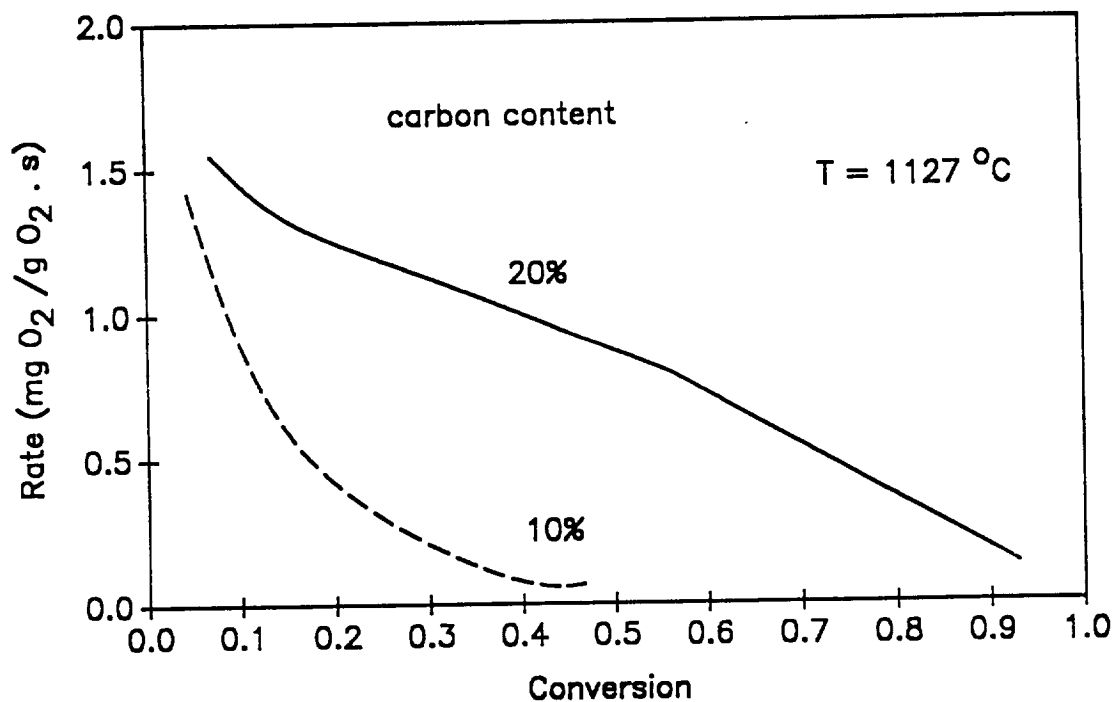
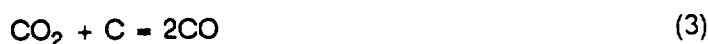
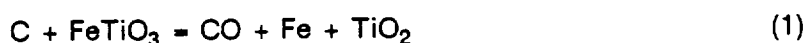


Figure 1.13. Effect of carbon content on ilmenite reduction kinetics.

Another important finding is the influence of carbon type on the kinetics of the process. As shown in Figure 1.14, the reaction rate and even product distribution for two types of carbon are quite different. It seems that carbon forms with higher surface activity give a higher overall reduction rate. These preliminary results indicate that the gasification of carbon is an important (and possibly rate-determining) step in the overall process. Therefore, the use of a catalyst to promote this reaction should be investigated. One of the objectives of this study is to find a suitable catalyst to promote the gasification reaction.

The chemical reactions taking place during the carbothermal reduction are as follows:



Reaction 1 is expected to start at the points of contact between carbon and ilmenite. However, the desirable path which will be emphasized in this project is a combination of Reactions 2 and 3. This path does not require solid contact and can use a wide variety of carbonaceous compounds for ilmenite reduction.

Finally, a new temperature and concentration-programmed reaction is being developed to investigate the mechanism of the reduction reaction. This technique is suitable for studying the effect of various reaction conditions on rate using relatively few experiments. One example showing the effect of temperature on rate is shown in Figure 1.15.

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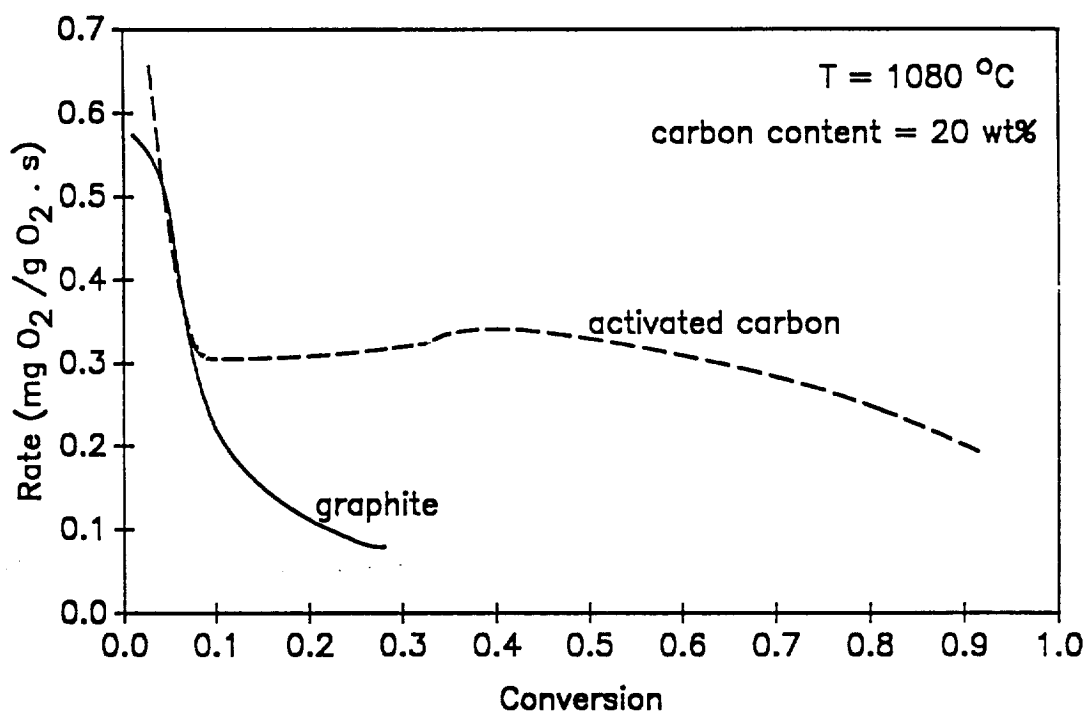


Figure 1.14. Effect of carbon type on ilmenite reduction kinetics.

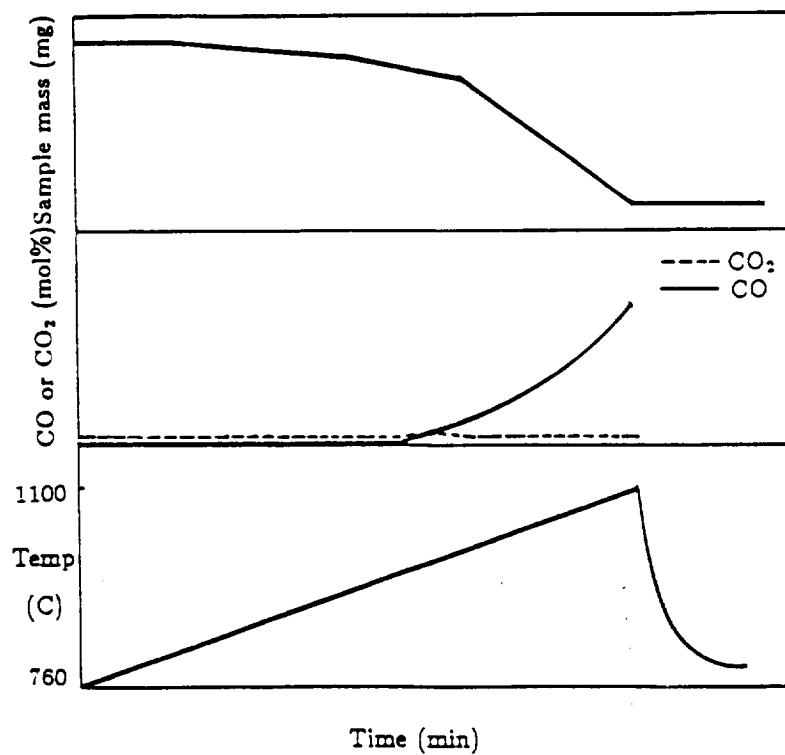


Figure 1.15. Temperature-programmed reaction results.

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